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Letter to the Editors

Triple point solid volume of polar liquids

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With increasing importance of theoretical investigations of thermodynamic properties for locating solid-liquid phase transition and examining melting behaviour, there is a growing need for the evaluation of triple point limiting solid volume of liquids. Recently, Sharma (1979) has proposed an analytical method of estimating limiting solid volume V_s of simple non-polar liquids in terms of characteristic volume V^*. As an extension to this method to include polarizable non-polar, polar and hydrogen-bonded liquids we modify the treatment and compute, in this paper, the values of V_s in case of the liquids having strong polar interactions.

For simple liquids, the characteristic volume V^* is given by (Sharma and Bhatnagar 1975)

$$V^* = aV_c \tag{1}$$

where $a = (p_c V_c / RT_c)$ is the critical state compressibility factor; p_c, V_c, T_c are critical constants and R is the universal gas constant.

Fang and Wiehe (1973) have suggested that V^* of any molecule may be expressed in terms of critical volume V_c of argon. In view of this proposal the resulting equation for a polar molecule can be written as

$$V^* = \tilde{a}\, aV_c = a^* V_c \tag{2}$$

in which

$$\tilde{a} = a^*/a. \tag{3}$$

where a^* is critical compressibility ratio of argon.

At the melting point the distances between nearest neighbours for unexpanded solid and liquid change only slightly inspite of total volume expansion on melting. However, the average number of nearest neighbours Z of a typical molecule may be slightly decreased (Einstein and Gingrich 1942, Henshaw 1957).

The effective coordination number Z' of a liquid for the solid phase at the melting point can be written as (Sharma 1979)

$$Z' = ZA \tag{4}$$

in which

$$A = ae \tag{5}$$

In equation (4) Z denotes the coordination number at absolute zero temperature and A is the proportionality constant (Sharma 1976) and e is the base of the natural logarithms.

For simple, slightly non-spherical and polarizable liquids, the expression for molar volume V_s of unexpanded solid at melting point/or triple point is given by (Sharma 1979)

$$V_s = 2^{\frac{1}{2}} A V^*. \tag{6}$$

Equation (6) cannot be used directly to calculate V_s of polar molecules because the nature of intermolecular interactions in polar molecules differs markedly with that in simple spherical (non-polar) molecules.

Using a method similar to that of Sharma (1979) for simple non-polar liquids, we obtain an alternative expression for Z' for polar liquids by introducing an approximation given by

$$\tilde{a}\, \sigma_0^3 Z' = \sigma^3 Z \tag{7}$$

where σ is the nearest neighbour distance of the lattice and σ_0 is equilibrium molecular diameter.

The molar volumes of solid and liquid at melting point may be related to molecular diameters by an expression given by (Sharma 1979)

$$V_s = 2^{\frac{1}{2}} V^* (\sigma/\sigma_0)^3. \tag{8}$$

From equations (4), (7) and (8) we can write the desired expression for V_s in case of hydrogen-bonded and polar liquids for the solid phase at the melting point as

$$V_s = 2^{\frac{1}{2}} B V^* \tag{9}$$

in which

$$B = \tilde{a}\, A = a^* e \tag{10}$$

It may be observed that expressions (2) and (9) for V^* and V_s, respectively, for polar liquids are obtained from those for simple liquids (equations (1) and (6)) only by introducing the parameter $\tilde{a}$.

Equation (6) has been utilized to estimate values of V_s for several simple, slightly polarizable non-polar liquids and equation (9) for hydrogen-bonded and polar liquids, respectively, for which experimental data were available. The estimated values of V^* from the experimental data on a^* (= 0·292), a and V_c quoted from Lange (1967), and Kobe and Lynn (1953) were obtained by using equation (2). Our calculated values of V_s in comparison with those reported in literature (Moolwyn-Hughes 1965, Eyring *et al* 1967, 1966) for slightly polarizable non-spherical liquids are shown in table 1 and for polar and hydrogen bonded liquids in table 2.

Table 1. Comparison of calculated and experimental values of V_s of slightly polarizable non-spherical liquids (Values of V_c V^* and V_s are given in cc mol^{-1})

Liquid	a	V_c	V^* calc.	V_s calc.	V_s exptl.
Ethylene	0·275	126·10	36·81	38·99	39·06
Benzene	0·265	256·00	74·66	76·14	77 00
Deuterium	0·310	59·98	17·52	20·86	20·48
Carbon tetrachloride	0·272	276 00	80·60	84·26	87·10
Chlorine	0·275	123·80	36·14	38 19	39·18
Bromine	0·288	135·40	39·55	43·77	41·58

Table 2. Comparison of calculated and experimental values of V_s of polar and hydrogen-bonded liquids (Values of V_c V^* and V_s are given in cc mol^{-1})

Liquid	a	V_c	V^* calc.	V_s calc.	V_s exptl.
Carbon monoxide	0·283	90·03	26·28	29·49	29·05
Methyl chloride	0·276	143·00	41·77	47·42	45·54
Water	0 243	58·80	17 17	19·27	19·82
Ammonia	0·244	72·00	21·02	23·59	22·32
Phosphine	0·273	113·30	33·11	37·14	41·44

It may be observed from tables 1 and 2 that the agreement between the calculated and observed values of V_s in almost all the liquids considered is very good, in view of the simplicity of the model and approximation. The present theoretical approach, although semi-empirical, is convenient and involves fewer experiments without introduction of any unjustified adjustable parameters. However, the calculated values are limited by the accuracy of experimental values of critical constants utilized in the model calculations.

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